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# NET METHYL MERCURY PRODUCTION VERSUS WATER QUALITY IMPROVEMENT IN CONSTRUCTED WETLANDS: TRADE-OFFS IN POLLUTION CONTROL

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*Abstract:* In a system with mercury contamination, there are trade-offs between beneficial functions of a wetland and environmental risk of methyl mercury (MeHg) production. This project used five wetland mesocosms with three different experimental designs to assess the potential for nutrient, sediment, and total mercury (THg) removal and MeHg production associated with a proposed a large-scale wetland system. The latter was suggested for the mouth of Steamboat Creek (Nevada, USA) at the confluence with the Truckee River. Steamboat Creek has been documented to have high mercury concentrations and is a major source of nutrients to the river. Mesocosms that had creek sediments as the base and creek water as inflows resulted in decreasing THg concentration by 72–82%. Average percent nitrogen and phosphorus and suspended solids removal were 43%, 30%, and 70%, respectively. Net MeHg production was observed during spring, summer, and fall months; however, in the winter, these mesocosms acted as a sink. One wetland mesocosm with sediments low in mercury and creek water showed similar trends. Mesocosms with creek sediments and water low in mercury were a source of MeHg year round, with outflow concentrations 10 to 200 times that in the inflow. Based on the developed data, the environmental risk of the proposed large-scale wetland would be an increase of methyl mercury concentration in creek water that reaches the Truckee River by as much as 20 to 75%. However, the wetland would also be a significant sink for nutrients, suspended solids, and total mercury, decreasing the amount of mercury available for methylation downstream.

*Key Words:* wetland mesocosms, mercury, methylation, nutrients

## INTRODUCTION

Steamboat Creek, Washoe County, Nevada, USA, is considered the most polluted tributary of the Truckee River and a major source of non-point pollution (Spurkland 2001). Since the Truckee River ends in the terminal Pyramid Lake, home to a fishery with one endangered and one threatened fish species, creek restoration is an important priority in the watershed. Restoration of Steamboat Creek has been the subject of much planning, and one proposed project included a large scale wetland at its confluence with the Truckee River (U.S. Army Corps of Engineers 2001). A wetland setting could provide the benefits of removing nutrients and suspended solids (Reed and Brown 1992, Spieles and Mitch 2000, Knowlton et al. 2002), reducing non-point source pollution.

High Mercury Hg concentrations have been documented in both creek water (24 to 419 ng/L; Lyons et al. 1998, Blum et al. 2001) and creek sediments (0.2 to 10.2 μg/g; Blum et al. 2001, Stamenkovic et al. 2004). Mercury in the creek is derived primarily from mine waste that has been distributed down the creek from the headwaters since the late 1800s. Approximately 80–90% of mercury transported by the creek is in the >0.45-μm fraction (Thomas 2003). The presence of mercury raises concern regarding wetland construction, for these ecosystems have been shown to be sites of exacerbated methyl mercury (MeHg) production (Zillioux et al. 1993, St. Louis et al. 1994, Rudd 1995, Morel et al. 1998, Branfireun et al. 1999). MeHg is toxic, readily bioaccumulated by aquatic organisms, and biomagnified in food webs (Boeing 2000, King et al. 2001). While wetlands usually act as sinks of total mercury (St. Louis et al. 1996, King et al. 2002), sediment biogeochemistry, nutrients, and anoxic conditions promote the activity of sulfate-reducing bacteria that methylate Hg (Compeau and Bartha, 1985, Zillioux et al. 1993, St. Louis et al. 1994, Matilainen

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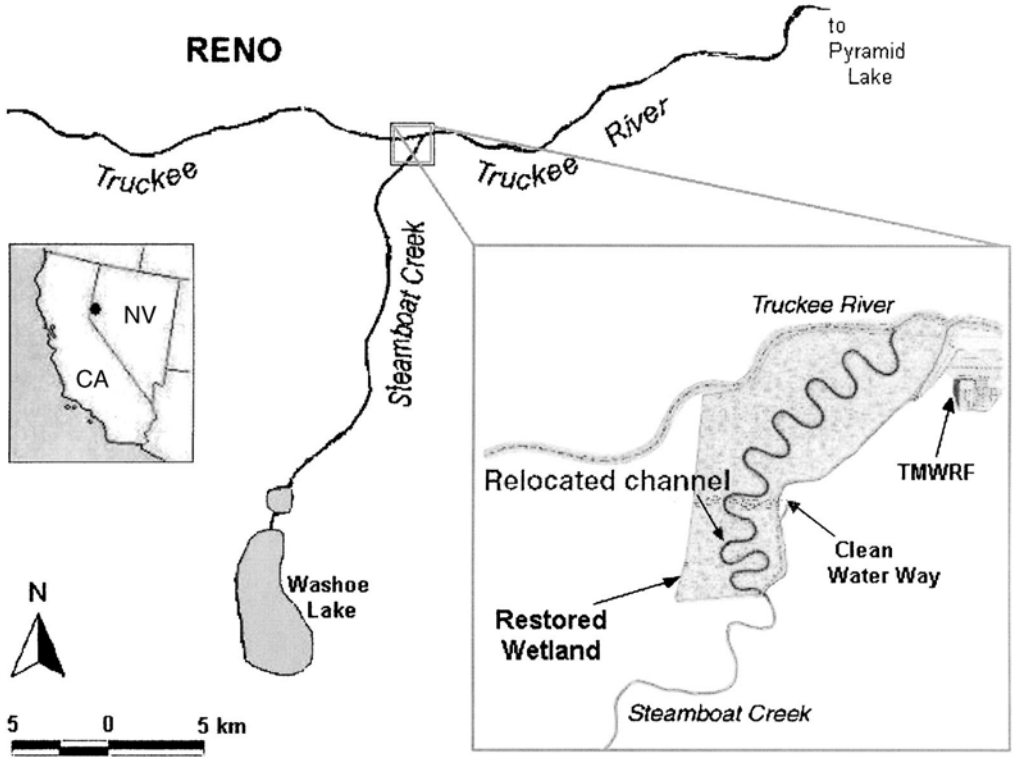


Figure 1. Steamboat Creek watershed. Insert shows the proposed location of the large-scale constructed wetland system and Steamboat Creek channel realignment; anticipated area of the reconstructed wetland is 0.34 km$^2$ (length 3700 m, width 210 m, sinusoid 2.3) (U.S. Army Corps of Engineers 2001, Spurkland 2001).

1995, King et al. 2000, Macalady et al. 2000). The contribution of MeHg from wetlands can be up to 80 times greater than from upland terrain per unit area (St. Louis et al. 1994).

In order to quantify anticipated nutrient removal within a wetland system at the mouth of the creek, two wetland mesocosms containing creek sediments (0.7 ± 0.6 μg g/L dry weight (dw)) and one containing clean sediments (low Hg: 0.1 ± 0.1μg/g dw), and using creek waters (25–318 ngHg/L) as inflows, were constructed on the stream bank above the mouth of Steamboat Creek (Spurkland 2001). This combination of water and sediments was thought to simulate the environmental conditions in the proposed wetland adequately. The data collected by Spurkland (2001) during the first year after construction showed that wetlands could significantly improve creek water quality by retaining almost 90% of total suspended solids, 70–80% of organic and inorganic nitrogen, and about a quarter of the phosphorus load. However, Hg monitoring was not done, and it was felt that in this contaminated watershed it should not be ignored.

In 2001, two additional mesocosms that contained creek sediments but used effluent from the Truckee Meadows Water Reclamation Facility, TMWRF (low Hg: 5 ± 1 ng Hg/L) were added to the experimental design. The water-treatment facility, which has tertiary treatment for nitrogen and phosphorus removal, discharges 1.1 × 10$^5$ m$^3$/day of treated water into Steamboat Creek. This design was believed to represent the wetland conditions in low water years when effluent and water diverted from the Truckee River may dominate channel flow. After these two additional mesocosms had equilibrated for six months, mercury monitoring began for all five mesocosms.

This study focused on assessing the potential for net methyl mercury production and total mercury removal in wetland mesocosms, in addition to monitoring nutrient-removal efficiency. This study was designed to collect empirical data that could help make management decisions regarding the risks and benefits of construction of a large scale wetland in a Hg-contaminated watershed.

## METHODS

### Wetland Mesocosms

This project used the five wetland mesocosms constructed in 2000–2001 (Spurkland 2001) near the confluence of Steamboat Creek and the Truckee River (Figure 1). The five parallel mesocosms (1.8-m wide,

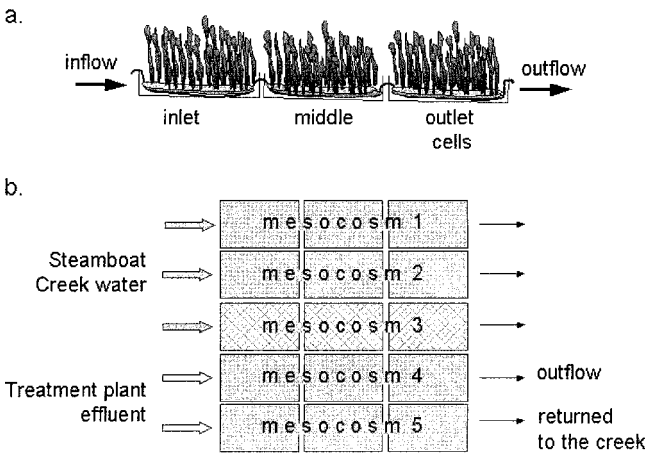


Figure 2. Experimental design for five wetland mesocosms. a. Cross section: water surface was exposed to the atmosphere, while water depths within each cell varied from approximately 5 to 20 cm. b. Experimental design: atop a base layer of 30 cm of aggregate and sand (mixed 80% sand and 20% aggregate by volume), autochthonous Steamboat Creek sediments were used in mesocosms 1, 2, 4, and 5. Mesocosms 1, 2, and 3 received water directly from Steamboat Creek (average flow 4.4 ± 2.3 L/min), while mesocosms 4 and 5 received treatment plant final effluent (average flow 4.1 ± 2.7 L/min).

9-m long and 0.6-m deep) had three equilength cells, each with a rubber liner, soil bottom, emergent vegetation, and a flow-through water system (Figure 2a). Plant cover was close to 100% in all cells. The dominant vegetation in all five mesocosms was cattails (*Typha* sp.), rushes (*Juncus* sp.), tall white top (*Lepidium latifolium* Linnaeus), and duckweed (*Lemna* sp.).

The experimental design was not optimal, with two replicated mesocosms for two experimental designs (creek water and sediments, and clean water and creek sediments) and one mesocosm with creek water and clean sediments. However, since this study was completed, the wetlands have been monitored continuously, and the trends in concentration differences between the inflow and outflow for each component discussed in this paper have been similar. This gives us confidence regarding the results discussed below, despite the limited replication.

## Sampling for Mercury Analyses

Water and sediment samples were collected bimonthly (January 2002–December 2002) using clean hands/dirty hands protocols (Gill and Fitzgerald 1987, Gill and Bruland 1990) into acid-washed Teflon® bottles (Keeler et al. 1995) for total mercury (THg) and MeHg analysis. Total and dissolved (beginning in May 2002) THg and MeHg in samples were determined for the inflow and outflow of each mesocosm.

All samples were preserved with optima hydrochloric acid (0.4%) and refrigerated until analysis. Sample filtration was done using a peristaltic pump, acid-cleaned Teflon tubing, and 0.45-μm Teflon® capsule filters. Filter blanks were obtained by filtering nanopure water in the field after sample collection, using the same configuration as other samples.

Surface-sediment samples (0–1 cm) were collected bimonthly from the inlet and outlet cells of each mesocosm. Subsamples from three different locations within a cell were pooled together, homogenized, and stored in the refrigerator in glass vials with Teflon lined lids until analysis (up to 28 days).

## Analytical Methods

Analyses of water and sediment samples for MeHg were completed immediately after sample collection (within 5–7 days). Extraction steps included acidic bromide/methylene chloride extraction and back extraction into water for sediment samples (Bloom et al. 1997) and distillation (Horvat et al. 1993) with matrix modification (Bloom and Von der Geest 1995) for water samples. Following the sample extraction, MeHg was determined using the aqueous phase ethylation procedure, isothermal GC separation, and cold vapor atomic fluorescence spectrophotometry (CVAFS) (Bloom 1989, Liang et al. 1994). Although the percent MeHg was relatively low in creek water (0.7 ± 0.3% of total and 1.8 ± 0.8% of dissolved), MeHg artifact production was considered to be small since MeHg and THg concentrations were not correlated. In addition, total organic carbon, which has been shown to result in generation of a MeHg artifact (Bloom et al. 1997), was low in creek water. Five-point calibration was done before and after daily analysis and verified every 10–12 samples using certified reference material (NIST-3133). Dogfish muscle standard (DORM-2) was used as an independent quality control sample (cf. Bloom et al. 1997, Marvin-DiPasquale et al. 2003), and measured concentrations were 120 ± 13% (n = 52) of the certified value. Analysis of triplicate samples yielded an average coefficient of variation (CV) of 18 ± 12% and 25 ± 16% for water and sediment samples, respectively. The methods detection limit based on three standard deviations of reagent blanks was 5 pg/L (n = 44) for a 50 ml sample. Although addition of ammonium pyrrolidine dithiocarbamate (1% APDC) was shown to improve distillation recoveries and reproducibility (Bloom and Von der Geest 1995), the recovery of spikes in nanopure water was lower than in matrix spikes. The average MeHg extraction efficiency was 82 ± 45% (n = 36) and 98 ± 47% (n = 22) for standard additions to nanopure water and water samples, respectively. The blank and matrix

Table 1. Total THg concentrations [ng/L] in mesocosm inflows (Steamboat Creek water, and treatment plant effluent), and outflows from wetland mesocosms fed by respective waters. Dissolved THg concentrations [ng/L] given in parenthesis starting in May 2002.

| | Steamboat Creek water | | | Treatment plant effluent | |
|---|---|---|---|---|---|
| | | Outflow | | | Outflow |
| Collection date | Inflow | Creek Sediments | Clean Sediments | Inflow | Creek Sediments |
| January 2002 | 46 | 10 | 8 | 4 | 42 |
| March 2002 | 76 | 18 | 16 | 8 | 25 |
| May 2002 | 115 (13) | 16 (10) | 23 (8) | 4 (5) | 15 (12) |
| July 2002 | 73 (17) | 23 (8) | 9 (8) | 6 (5) | 72 (11) |
| August 2002 | 49 (10) | 13 (8) | 11 (4) | 6 (5) | 13 (8) |
| October 2002 | 25 (4) | 4 (4) | 5 (4) | 5 (4) | 6 (5) |
| December 2002 | 318 (24) | 95 (24) | 100 (28) | 4 (3) | 4 (3) |

spike recoveries were 88 ± 43% (n = 14) and 93 ± 41% (n = 10) for sediment samples.

Total Hg in water was determined by bromine monochloride oxidation followed by stannous chloride reduction and purging of elemental mercury from solutions onto gold-coated quartz sand traps (Bloom and Crecelius 1983). Mercury on traps was determined using dual amalgamation and CVAFS (Dumarey et al. 1985, Bloom and Fitzgerald 1988). All samples were analyzed in triplicate, and average CV was 9 ± 6%. The method detection limit for THg in water was 0.4 ng/L for a 100-ml sample, based on three standard deviations of sample blanks (n = 16). Total mercury analysis of sediments was done with a solid state Milestone™ Mercury analyzer (EPA method 7473). Certified reference materials (NIST-2709, NIST-1547, NIST-1515) were analyzed each time, and errors were less than 5%. All samples were analyzed in triplicate, and average CV was 12 ± 8% for replicate sediment samples.

### Water Quality Measurements

Water quality samples were collected biweekly at the same time of the day to minimize potential variations resulting from diurnal cycles. Physical parameter data collected *in situ* from the inflow pipes and from the outflow of each mesocosm consisted of dissolved oxygen (DO) (Yellow Sweet Instruments, Model 59), temperature (YSI, Model 30), pH (Orion Instruments, Model 290A), and flow. All field instruments were calibrated in the laboratory before each sampling period. At the same time, water samples were collected for analysis of total suspended solids (TSS) (Standard Method 2540D), total organic carbon (TOC) (UV-persulfate method), total Kjeldahl nitrogen (TKN) (QuickChem 8000 automated analyzer), nitrite plus nitrate nitrogen ($NO_2^- + NO_3^-$) (EPA certified Standard Methods 4500B and 4500E), total phosphorus (TP), and orthophosphate (OP) (Standard Methods 4500P-B, and 4500P-E, respectively) (by A. Gupta and K. Dennett). Loss on ignition (LOI) was determined using approximately 0.2 g sediment subsamples that were oven-dried in ashed aluminum boats overnight at 105°C to constant weight. After recording the dry weight, samples were combusted at 540–550°C in a muffle furnace for two hours to estimate the organic content of the sediments (Heiri et al. 2000). All samples were cooled to room temperature in a desiccator before any weights were recorded.

Total and methyl mercury data for water and sediments in different wetland mesocosms were compared using t-test analysis (MINITAB® Release 13.32 for Windows). The strength of relationship between MeHg net output and physical parameters and nutrient concentrations was evaluated using Pearson correlation. Results were considered statistically significant at $p < 0.05$.

## RESULTS

### Total Mercury in Water

Data collected over one year showed that THg was consistently removed from the creek water passing through wetland mesocosms (Table 1). Total THg concentrations in creek water varied at each sampling, and most Hg was particulate-bound (84 ± 6%). The overall removal efficiency for THg in the mesocosms fed by creek water ranged from 72 to 82%, which was mostly due to deposition of particulate-bound THg (removal of dissolved THg was on average 24%). In contrast, treatment-plant effluent contained mostly dissolved THg (89 ± 13%), and THg concentrations did not change much throughout the year (Table 1). Wetland mesocosms fed by plant effluent were a significant source of THg, mostly due to net export of particulate-bound THg.

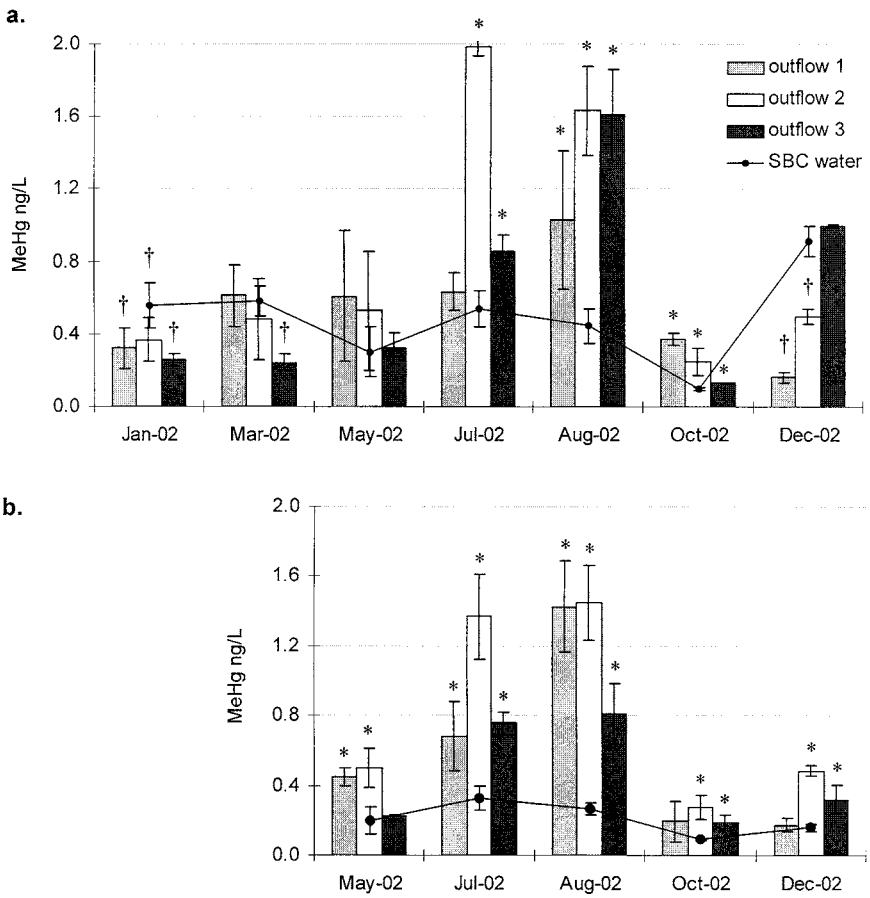


Figure 3. Average total (a) and dissolved (b) MeHg concentrations in Steamboat Creek water and outflows from mesocosms fed by creek water. Error bars represent the standard deviation of three replicates. Asterisk (*) denotes that the outflowing waters had significantly higher (t-test, $p < 0.05$) concentration of MeHg (wetland mesocosms were a net source of MeHg); (†) indicates that MeHg concentration in outflow was lower (t-test, $p < 0.05$) than in Steamboat Creek water.

## Methyl Mercury in Water

Total MeHg concentrations were monitored over the same time period as THg. Typically, wetland mesocosms fed by creek water were a source of total and dissolved MeHg in summer and fall (Figure 3) and a net sink for total MeHg in winter months (Figure 3a).

Although the total MeHg concentration in the treatment plant effluent was lower than in creek water, both total MeHg and dissolved MeHg concentrations in outflows from mesocosms fed by plant effluent were significantly higher than the respective concentrations in outflows from mesocosms fed by creek water and significantly higher than the inflowing plant effluent (Figure 4). These mesocosms were a source of MeHg year round.

Percent THg as MeHg was 0.7 ± 0.3% in creek water and 2.2 ± 2.2% in plant effluent effluent. Average % MeHg in outflows from mesocosms fed by creek water was 5.1 ± 4.3% and 18.2 ± 13.0% in mesocosms fed by plant effluent.

## Mercury in Sediments

Average THg content in sediments in inlet cells of mesocosm fed by creek water (0.6 ± 0.6 μg/g dw) was greater than in outlet cells (0.3 ± 0.2 μg/g dw). Although a similar pattern was observed in mesocosms fed by the treatment-plant effluent (1.0 ± 0.8 μg/g dw, and 0.8 ± 0.6 μg/g dw, respectively), the difference was not significant. The mesocosm that originally contained low Hg sediment had a somewhat lower THg concentration in sediments than mesocosms with autochtonous creek sediments; however, this difference was significant only in outlet cells, with inlet cells having similar THg concentrations.

No seasonality was observed in the sediment MeHg content. MeHg in sediments ranged from 0.01% to 1.43% of total mercury. The average percent MeHg of THg in inlet cells of all five mesocosms was 0.3 ± 0.1%, while in the outlet cells of mesocosms with the creek sediments as a base, it was 0.2 ± 0.1%. In the outlet cell of the mesocosm with clean sediments, on

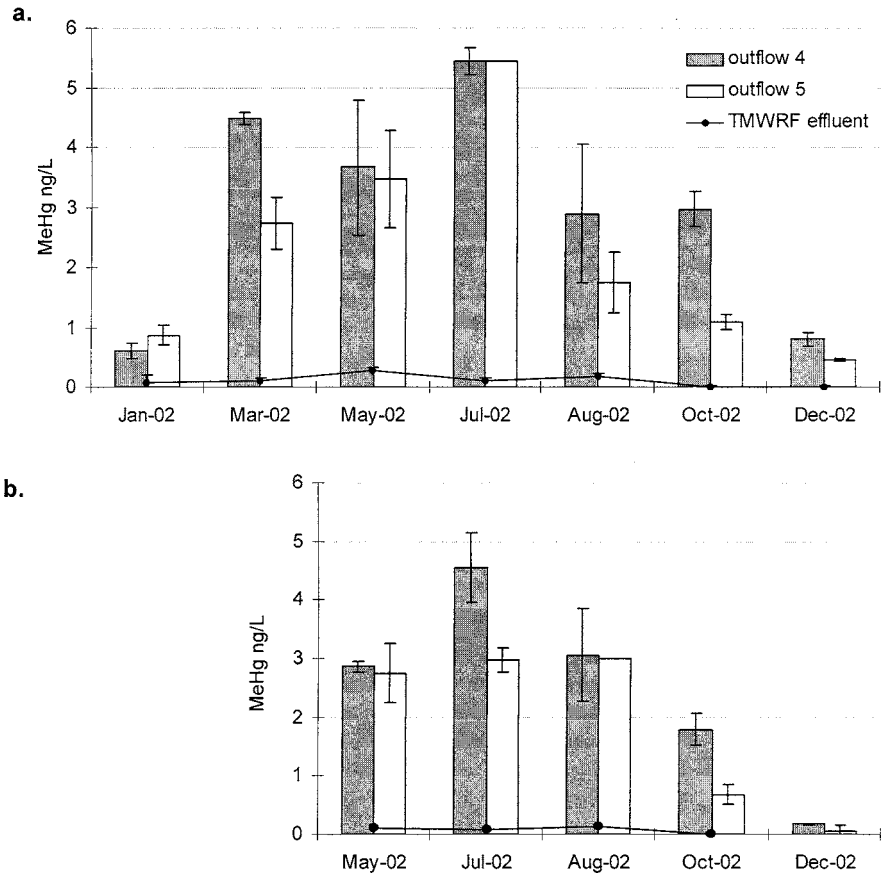


Figure 4. Average total (a) and dissolved (b) MeHg concentrations in treatment-plant effluent and outflows from mesocosms fed by the effluent. Error bars represent the standard deviation of three replicates. Concentrations of total (unfiltered) and dissolved (filtered) MeHg in outflowing waters were significantly higher (t-test, $p < 0.05$) than in the inflowing treatment plant effluent.

average MeHg accounted for 0.6 ± 0.5% of the total mercury.

### Water Quality

Most water quality parameters measured for Steamboat Creek water and the treatment-plant effluent differed significantly (Table 2). However, temperature and dissolved oxygen behaved similarly in all five mesocosms and showed seasonality. Outflow temperatures were, on average, 3–4°C lower than inflow temperatures, and DO at the outflow was, on average, depleted by 2 to 3 mg/L.

Nutrients and suspended solids were retained within the wetland mesocosms (Table 2). The wetland mesocosm with clean sediments was better at removing inorganic nitrogen than mesocosms with the creek sediments. Total phosphorus (TP) concentrations in creek water and plant effluent were similar, but the removal efficiency was better in the three mesocosms fed by the creek water. Mesocosms fed by creek water removed total suspended solids efficiently, while there was some net export of TSS from the mesocosms fed by the plant effluent. All five wetland mesocosms had similar average removal efficiency for total organic carbon.

Net MeHg export from mesocosms fed by the creek water was correlated with more water quality parameters than export of MeHg from mesocosms fed by treatment-plant effluent (Table 3).

## DISCUSSION

Wetland mesocosms fed by the Steamboat Creek water efficiently removed THg from the water column. In all mesocosm cells, Hg deposition to the sediments was an important input to the system, and more Hg was deposited as the water first entered the mesocosm, as demonstrated by the fact that THg concentrations in inlet cell sediments were greater than those in outlet cells. Inlet-cell sediments also had higher sediment MeHg concentrations than outlet cells, although the reverse might have been expected based on the organic content of the sediments (estimated as LOI) that was

Table 2. Inflow water characteristics for the wetland mesocosms studied: Steamboat Creek water and treatment-plant effluent, and respective concentration reduction.** Values are means of 23 samples collected biweekly for the duration of the study.

| | pH* | DO* | $NO_2^- + NO_3^-$* | TKN* | TP | OP | TSS* | TOC* |
|---|---|---|---|---|---|---|---|---|
| Creek water | 8.3 ± 0.4 | 8.92 ± 2.36 | 0.40 ± 0.16 | 0.90 ± 0.34 | 0.23 ± 0.07 | 0.19 ± 0.05 | 29.30 ± 14.60 | 4.98 ± 1.91 |
| % concentration reduction | | | 51 ± 30% | 25 ± 32% | 30 ± 21% | 32 ± 23% | 76 ± 13% | 10 ± 19% |
| % concentration reduction (mesocosm with clean sediments) | | | 79 ± 30% | 30 ± 30% | 37 ± 18% | 44 ± 28% | 69 ± 18% | 9 ± 15% |
| Plant effluent | 7.5 ± 0.3 | 6.49 ± 5.27 | 0.06 ± 0.13 | 1.53 ± 0.58 | 0.22 ± 0.14 | 0.15 ± 0.15 | 5.20 ± 2.52 | 9.48 ± 3.99 |
| % concentration reduction | | | † | 21 ± 17% | 20 ± 24% | 3 ± 47% | † | 15 ± 29% |

* Two sample t-test indicated significant ($p < 0.05$) differences between creek water and plant effluent parameters.
** Average percent reduction in concentration between mesocosm inflow and outflow.
† Variable percent concentration reduction and, on average, net export from the mesocosms.

higher in the outlet cells and DO that was depleted in outflows. MeHg concentrations in mesocosm sediments (0.01 to 12.2 ng/g) were comparable to the observed concentrations in sediments along Steamboat Creek in previous studies (0.03 to 12.9 ng/g) (Blum et al. 2001, Stamenkovic et al. 2004).

An estimated average annual amount of THg input to the Truckee River (based on the recorded THg concentrations in Steamboat Creek in this study and using the average flow over 25 years; USGS, 1975–1999) is 4.6 kg, or 12.7 g/day. This is higher than estimated annual mercury loading at Clean Water Way (just upstream from the TMWRF; Figure 1) of 1.45 kg for 1993, which was a low water year (Lyons et al. 1998), but similar to a calculated September 1999 loading of 16 g/day, which was a wetter than average year (Blum et al. 2001). Since most of the Hg transported by the creek is particulate-bound and the wetlands were a sink for suspended solids as well as THg, an estimated reduction of Hg amount transported to the river with a wetland at the mouth of the creek would be 3.3 to 3.8 kg/year, based on the calculated removal-efficiency range.

Net MeHg output in all five mesocosms was seasonal, peaking in the summer months (Figures 3 and 4). Higher MeHg concentrations in summer are attributed to increased microbial activity (Ullrich et al. 2001, King et al. 2002), while lower temperatures and senescent vegetation during winter may lower overall microbial activity and methylation (Gilmour et al. 1998). In addition, low temperatures favor demethylation (Ullrich et al. 2001), which can decrease the net export due to degradation of MeHg.

Although THg inputs were large in mesocosms fed by creek water, net MeHg output was similar compared to other systems. For example, peatland water and boreal catchments at the Experimental Lakes Area (St. Louis et al. 1996, Kelly et al. 1997, Branfireun et al. 1999), three Finnish lakes (Verta et al. 1994), and the Everglades (Stober et al. 1995) had THg concentrations an order of magnitude lower than outflow from wetland mesocosms fed by creek water but comparable concentrations of MeHg.

To estimate net annual MeHg output from the wetland mesocosms in this study, an area under the curve representing the net MeHg production was calculated using an average flow of 5 L/min and a mesocosm area of 16.2 $m^2$. The net annual MeHg production rate was calculated to be 15 to 55 $\mu g\ m^{-2}\ year^{-1}$ in the mesocosms fed by creek water, while in mesocosms fed by the treatment-plant effluent, it was estimated to range from 340 to 480 $\mu g\ m^{-2}\ year^{-1}$. These calculated rates were used to estimate the output of MeHg, assuming that such a system would be operated similarly to the mesocosms in this study and that MeHg output

Table 3. Pearson correlation coefficients for MeHg concentration in outflows from respective wetland mesocosms (corresponding p-values for the individual hypothesis tests of the correlations being zero are given in parenthesis).* Subscripts denote inflow (i), outflow (o), or removal efficiency (%).

| Mesocosm | $MeHg_i$ | Sediment THg (inlet) | $T_i$ | $T_o$ | $DO_o$ | $NO_3^-{}_i$ | $TSS_i$ | $TSS_{\%}$ |
|---|---|---|---|---|---|---|---|---|
| **1, 2, 3** | | 0.51 | 0.67 | 0.58 | −0.50 | −0.70 | −0.44 | −0.43 |
| | | (0.02) | (0.00) | (0.01) | (0.02) | (0.00) | (0.05) | (0.05) |
| **4, 5** | 0.53 | | | 0.60 | | | | |
| | (0.05) | | | (0.02) | | | | |

* Only statistically significant ($p < 0.05$) correlations are shown.

would be comparable to that of mesocosms fed by creek water. The average flow of the creek over 25 years was used and an area of 0.34 $km^2$ as a predicted area of the large-scale wetland system (length 3700 m, width 210 m, sinusoid 2.3) (Spurkland 2001). The additional net contribution of MeHg from a large-scale wetland to the Truckee River was estimated to range from 5 to 19 g/year. The amount of MeHg transported from Steamboat Creek to the Truckee River, without the large-scale wetland, using the 1.7 $m^3/s$ average flow and MeHg concentrations recorded in this study, was estimated to be 25 g MeHg per year. Thus, the proposed large-scale wetland could significantly increase the loading of MeHg to the Truckee River by as much as 20 to 75%. This is comparable to catchments containing valley bottom and riverine wetlands at the ELA that exported 22 to 100% more MeHg than inputs in 1991/1992 and 1992/1993 (St. Louis et al. 1996).

In spite of low concentration of THg and MeHg in treatment-plant effluent, MeHg output was significantly greater in the wetland mesocosms fed by the effluent relative to those fed by creek water. This implies that water chemistry is affecting methylation. For example, much of the THg in creek water was particulate-bound, which is of limited bioavailability. Additionally, creek water, which was high in nitrates, pH, and TSS content (Table 2), might have generated a suboptimal environment for methylating bacteria. The creek water had a significantly greater TSS content than plant effluent, and particulate matter has been shown to suppress methylation in water strongly (Matilainen and Verta 1995). The increased deposition due to settling of the particulate matter might have included organic compounds as well, resulting in some particulate-bound MeHg being retained within the wetland. This is further supported by correlation analysis that showed a weak negative correlation between the MeHg concentrations in outflows from mesocosms fed by creek water and the inflow TSS content and with the removal efficiency of TSS in these mesocosms (Table 3).

In addition, nitrates have been shown to inhibit methylation (Steffan et al. 1988). Amendment experiments to sediment cores from the Florida Everglades demonstrated that elevated nitrate concentration significantly lowered methylation rates (about 10 times) relative to unamended cores (Gilmour et al. 1998). Field data from the Everglades also showed that more pristine areas (with less $NO_3^-$) had higher methylation rates (Gilmour et al. 1998). In the small-scale constructed wetland situation, mesocosms fed by treatment-plant effluent had significantly less nitrates than mesocosms fed by creek water (Table 2).

Water pH can also affect mercury methylation, enhancing production at low pH, and inhibiting production at higher values (Ullrich et al. 2001). Although creek water had higher pH than plant effluent (Table 3), neither one was as acidic as the values recorded to be ideal for methylation, around pH of 5 (Ullrich et al. 2001). Some difference might have occurred due to pH, but the observed trend in the wetlands cannot be explained fully based on this parameter.

MeHg export from mesocosms fed by creek water was correlated with factors previously demonstrated by others to affect MeHg formation. A positive correlation was observed between MeHg flux from the wetlands and temperature, similar to small forest lakes in Finland (Verta et al. 1994). A negative correlation was found between MeHg and DO, as expected, for methylation is favored under reduced conditions. A negative correlation of MeHg with nitrates (Steffan et al. 1988, Gilmour et al. 1998) and TSS (Matilainen and Verta 1995) was also observed in wetland mesocosms fed by creek water. MeHg concentrations in the outflowing water were negatively correlated with water pH, but this relationship was not statistically significant ($r = -0.37$, $p = 0.10$).

Overall, the observed concentration reductions between inflows and outflows for mesocosms fed by the creek water (Table 2) were comparable to average combined performance data for surface- and subsurface-flow wetland treatment systems in North America (Kadlec and Knight 1996). One concern with con-

structed wetlands is their ability to remove phosphorus over time (Craft 1997). In the third year of operation, wetland mesocosms with creek water remained efficient at nutrient- and sediment-removal. Orthophosphate and total phosphorus concentrations in creek water, and corresponding removal efficiencies for these nutrients monitored in 2000 and 2001 (Spurkland 2001), were similar to those observed in this study. The concentration reduction values for OP and TP were similar to the recorded ranges for treatment wetlands in North America (37% and 32–57%, respectively) (Kadlec and Knight 1996). Inorganic and organic nitrogen concentrations and TSS content were similar to previously recorded values for creek water (Spurkland 2001). The removal efficiencies for $NO_2^-$ + $NO_3^-$, TKN, and TSS in mesocosms fed by creek water were lower compared to the performance in 2000 and 2001 (Spurkland 2001) but were still comparable to the average performance of treatment wetlands in North America: 61–69% and 43–50% removal for $NO_2^-$ + $NO_3^-$ and TKN, respectively, and 70–79% for TSS (Kadlec and Knight 1996).

## CONCLUSIONS

Decisions regarding construction of a wetland at the mouth of Steamboat Creek or within any Hg-contaminated watershed must weigh all the risks and benefits, including habitat and ecosystem restoration and preservation, non-point-source nutrient removal, methyl mercury production, human and ecological health impacts, and economical impacts. With deposition of 72 to 82% of stream-transported THg in the wetland (removing 3.3 to 3.8 kg of THg annually), the amount of Hg available for methylation downstream would probably decrease. This reduction of Hg pollution to downstream ecosystems is important to consider. It has been shown that mercury concentrations in fish in the Truckee River increased downstream from the confluence with Steamboat Creek, suggesting that particulate bound mercury could be methylated in river settings (Gustin et al. 2005). In addition, improvements in water quality through nutrient- and suspended-sediment-removal need to be considered as positive impacts of a constructed wetland. However, the presence of a wetland could increase the loading of MeHg from Steamboat Creek into the Truckee River by as much as 20 to 75%. This study provides important empirical data that can be used by watershed managers in assessing the potential trade offs and environmental consequences of wetland construction in a mercury-contaminated watershed.

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